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Influence of sericin/TiO_2 nanocomposite on cotton fabric: Part 1. Enhanced antibacterial effect

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ABSTRACT

Sericin as a biological material was extracted from raw silk by boiling in hot water and nano-TiO_2 was dispersed in its solution. The prepared finishing agents with and without polycarboxylic acid cross-linking agents were treated on cotton fabric using pad-dry-cure. Presence of sericin, nano-TiO_2, and cross-linking agents on cotton fabric was confirmed by at least one of the following experimental FTIR, SEM, EDX, and XRD. The antibacterial activity and the durability of modified cotton fabrics were investigated against one Gram-positive bacterium (*Staphylococcus aureus*) and one Gram-negative bacterium (*Escherichia coli*). The finishing treatment on the cotton fabric was more effective against *S. aureus* than *E. coli*. The fabrics treated with nano-TiO_2 were possessed more activity against bacteria as compared to sericin and also considerably improved with given nanocomposite. The antibacterial activity of treated fabrics with cross-linking agents has not been considerably changed after 20 and 40 launderings. The fabrics treated with given nanocomposites did not dramatically affect the breaking strength.

1. 1. Introduction

Almost all antimicrobial agents used in commercial textiles are synthetic materials and biocides that damage the cell wall or alter cell membrane permeability, denature proteins, inhibit enzyme activity or prevent lipid synthesis, all of which are essential for cell survival (Gao & Cranston, 2008; Gouveia, 2010). However, many of these chemical agents are toxic to humans and do not easily degrade in the environment. Hence, there is a great demand for antimicrobial textiles based on non-toxic bioactive compounds (Joshi, Wazed, Purwar, & Rajendran, 2009; Shi, Zhao, Zhang, Su, & Tan, 2008).

Sericin is a hot water-soluble macromolecular globular protein. It envelops the fibroin filament with successive sticky layers that helps in the formation of cocoon and contributes about 20–30% of the total cocoon weight (Sasaki, Kato, Watanabe, & Yamada, 2000; Sasaki, Yamada, & Kato, 2000; Voegeli, Meier, & Blust, 1993). The sericin protein is made of 18 amino acids most of which have strongly polar side groups such as hydroxyl, carboxyl, and amino groups (Gulrajani, 1993; Gulrajani & Gupta, 1989, chap. 7; Tortman, 1993, chap. 8) that enable easy cross-linking, copolymerization, and blending with other polymers to form improved biodegradable materials (Zhang, 2002). It is a degradable biomaterial with different physiological properties, such as antibacterial activity, antioxidant, ultraviolet protection, moisture absorption, and biocompatibility properties (Gulrajani, Brahma, Kumar, & Purwar, 2008). It has been used on textiles to enhance moisture absorption, antistatic properties, softness, and comfort (Gulrajani et al., 2008; Kongdee, Bechtold, & Teufel, 2005; Kongdee & Chinthawan, 2007; Lee, Miyazaki, Hisada, & Hori, 2004). It has been applied on polyamide or polyester fibers to obtain antioxidant and antimicrobial activity using as indoor air filters to decrease free radicals and fungi or bacteria contaminations (Sarovart, Sudatis, Meesilpa, Grady, & Magaraphan, 2003). Furthermore, it can prevent abrasive skin injuries and rashes, and enhance tear resistance, crease recovery, and dye ability to direct dye (Kongdee et al., 2005). Sericin has adhesive property and affinity to keratin due to its chemical composition (Voegeli et al., 1993). It has also grafted into wool fiber to improve fiber strength, shrinkage resistance, and softness (Cortez, Anghieri, Bonner, Griffin, & Freddi, 2007). To improve the washing durability of antibacterial finishing, citric acid (CA) and 1,2,3,4-butane tetra carboxylic acid (BTCA) are mentioned as eco-friendly cross-linking agents (Nazari, Montazer, Rashidi, Yazdanshenas, & Moghadam, 2010; Orhan, Kut, & Gunesoglu, 2009).

Montazer et al. have studied many works in the field of textile processing especially finishing and dyeing with inorganic nanoparticles such as nanosilver and nano-TiO_2 (NTO) and

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biopolymers such as chitosan (Barani, Montazer, Samadi, & Toliyat, 2012; Harifi & Montazer, 2012; Montazer, Alimohammadi, Shamei, & Rahimi, 2012a, 2012b; Montazer & Pakdel, 2011; Nazari, Montazer, Moghadam, & Anary-Abbasinejad, 2011). In this investigation, sericin extracted from raw silk filaments with hot water due to its simplicity without further purification (Oh, Lee, Kim, Um, & Lee, 2011). Aqueous dispersion of NTO and its composite with sericin were prepared. Two cross-linking agents CA and BTCA were chosen with sericin, NTO, and nanocomposite to produce fabrics with durable antibacterial activity. The presence of chemicals on the cotton fabric was confirmed by at least one of the testing analyses including FTIR, SEM, EDX, and XRD. The TEM was employed to determine the NTO particle size and to study the morphology and agglomeration of nanoparticles present in nanocomposite.

Composite of NTO and sericin was expected to have "synergistic effect" for diverse physiological properties, such as ultraviolet protection, moisture absorption, self-cleaning, wrinkle recovery, and antibacterial activity properties. The objective of the present study was to investigate the antibacterial activity of modified cotton fabrics against two bacteria strains and laundering fastness of the finished fabrics. Finally, the optimal conditions for antibacterial activity were predicted by Response Surface Methodology (RSM).

2. Experimental

2.1. Materials

Scoured, and bleached plain weave cotton fabric with 115 g/m^2 were used. All chemicals were of analytical reagent grade. Twice-distilled water was used throughout the experiments. Sodium hydroxide, hydrogen peroxide, CA, BTCA, sodium hypophosphite (Merck, Germany) and dispersing agent under the trade name Dyasol 50L (Dyer Chemie, Iran) were used without further purification. Sericin powder was prepared from degummed solution by evaporation. NTO powder under the trade name AEROXIDE P25, was kindly gifted by Evonik Degussa Corporation with nanoparticles range from 20 to 30 nm in diameter. Microorganisms used in the study were *Staphylococcus aureus* (ATCC 6538) as a model for Gram-positive bacteria and *Escherichia coli* (ATCC 11303) as a model for Gram-negative bacteria. The strains were all cultured on tryptic soy agar (TSA) (Merck, Germany).

2.2. Methods

2.2.1. Preparation of sericin powder

Raw silk filaments were purchased from a local silk manufacturer (Kashan, Iran), washed twice with distilled water and dried at 35 °C for 24 h. The cleaned raw silk filaments were cut into short fragments with average length of 20 mm. The aqueous extraction of sericin was carried out through the boiling of the raw silk in distilled water for 90 min with 30:1 liquor-to-material ratio. The aqueous solution obtained was collected and filtered through filter paper (Whattman) to remove the impurities and fibroin. The degumming solution was concentrated by vaporizing water under steam heating and dried on a tray under steam, ground into powder and then used without any purification for preparing sericin solution and nanocomposite of sericin/NTO.

2.2.2. Preparation of NTO and nanocomposite aqueous dispersion

NTO suspension was prepared by dissolving dispersing agent (2%, w/w, on weight of NTO) in adequate distilled water and NTO powder was then added gradually while stirring. NTO was suspended partially and the obtained system was unstable. Hence, probed homogenizer (Sonopuls Ultrasonic Homogenizer, Bandelin Co., Germany, model HD 3200) was employed for 45 min to produce a thoroughly homogeneous dispersion system and stable for relatively long time (at least one month). The obtained sericin powder was dissolved in distilled water under steam heating and then cooled to room temperature. For nanocomposite dispersion, NTO colloidal suspension was added dropwise to the sericin solution. The mixture was left under stirring for 15 min at room temperature. The prepared nanocomposite was more stable when compared with NTO suspension. The appropriate content of NTO and sericin powder was prepared according to experiment requirements.

Table 1
CCD experimental design for treated cotton with sericin, NTO, and nanocomposite along with CA or BTCA.

Run[a]	Sample code[b]	NTO (g/L)	Sericin (g/L)	CA or BTCA (g/L)
1, 18	N2S2X1	50	50	25
2, 19	N1S1X1	25	25	25
3, 20	N0S1X2	0	50	25
4, 21	N1S0X0	25	0	0
5, 22	N1S1X1	25	25	25
6, 23	N2S1X2	50	25	50
7, 24	N0S1X0	0	25	0
8, 25	N1S1X1	25	25	25
9, 26	N0S2X1	0	50	25
10, 27	N2S1X0	50	25	0
11, 28	N1S0X2	25	0	50
12, 29	N1S2X2	25	50	50
13, 30	N2S0X1	50	0	25
14, 31	N0S0X1	0	0	25
15, 32	N1S1X1	25	25	25
16, 33	N1S1X1	25	25	25
17, 34	N1S2X0	25	50	0

[a] Runs 1–17: samples treated with CA and runs 18–34: samples treated with BTCA.
[b] X: cross-linking agents; CA or BTCA.

2.2.3. Statistical analysis

The experimental design chosen for this study was the central composite design (CCD) and then was performed by RSM. This design was a full factorial design with all combinations of the factors at two levels (high, +1, and low, −1). Four variables including the amounts of BTCA, CA, sericin, and NTO were studied. The ranges of these variables were at concentrations of 0–50 g/L. Details of the central composite design for various samples are presented in Table 1. The total number of test runs needed for this design was 34.

The antibacterial activity was assessed based on percentage of bacterial reduction for different experimental designs. RSM was applied to analyze the effect of independent variables (concentration of BTCA, CA, sericin, and NTO) on the response parameter (percentage of bacterial reduction) by matching the response studied (Y) with the code factors using the polynomial model associated with the experimental design as defined in Eq. (1).

$$Y = A_0 + \sum A_i \cdot X_i + \sum A_{ii} \cdot X_i^2 + \sum A_{ij} \cdot X_i \cdot X_j \quad i \geq j \tag{1}$$

where Y is the dependent variable, A_0 is the constant coefficient, A_i is the linear coefficient, A_{ii} is the quadratic coefficient, and A_{ij} is the two factors interaction coefficient.

2.2.4. SEM/EDX

The surface morphologies of the untreated and treated cotton fabrics were observed with a scanning electron microscope (LEO 440i, UK) equipped with energy dispersive X-ray facility to investigate the chemical composition of the coatings on treated cotton fabrics for elements having atomic number greater than sodium. The standard procedure was followed, in which samples for SEM and EDX analyses were coated with a gold layer before tests to ensure sufficient electrical conductivity and to prevent charging effects.

2.2.5. TEM

TEM images were obtained on a Philips EM208, using an accelerating voltage of 100 kV. NTO powder was dispersed in ethanol for TEM observation using an ultrasonic bath (Bandelin Co., Germany, model DT 514 BP). A drop of the sample suspension was dried on a carbon coated copper grid, observed under TEM and then shape and size of NTO were characterized.

2.2.6. XRD

X-ray diffraction patterns of treated and untreated cotton fabrics and the crystalline of NTO were measured by X-ray diffraction spectroscopy (3003 PTS, SEIFERT, Germany). The patterns were recorded in the diffraction range of 2θ from angle of 10° to 50° with a scanning speed of 2°/min at 2θ step of 0.040°. Cu Kα radiation ($\lambda = 0.154060$ nm) with detector scan mode operating at 40 kV and 30 mA was used to investigate changes in crystalline.

2.2.7. FTIR

Fourier transform infrared spectroscopy was performed with a Thermo Nicolet 6700 FTIR spectrometer (Thermo Electron Co., USA) and the measurements were carried out by using KBr pellets. The spectra were recorded over the range 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}.

2.2.8. Treatment of cotton fabrics with prepared finishing agents

The bleached cotton fabrics cut in sizes of 30 cm × 20 cm. Cotton fabrics were independently impregnated in finishing solutions containing sericin with concentration range (0–50 g/L), NTO (0–50 g/L), and their combination at room temperature for 20 min, padded through squeeze rollers with single dip and single nip to give a wet pick up of 100 ± 5% o.w.f. and dried at 100 °C for 5 min in a preheated oven. Afterwards, some treated cotton samples were immersed in aqueous treatment baths containing CA or BTCA and sodium hypophosphite (SHP). The finishing solutions were prepared as displayed in Table 1. The fabrics treated with different concentrations of CA or BTCA (0–50 g/L) were padded through squeeze rollers with single dip and single nip to give a wet pick up of 100 ± 5% o.w.f. which SHP as a catalyst of polycarboxylic acids was used 60% on weight of cross-linking agent. The padded samples were dried at 100 °C for 5 min and then cured in a laboratory oven under suitable conditions with respect to cross-linking agent (150 °C, 5 min for CA and 180 °C, 2 min for BTCA (Nazari et al., 2010)). The finished fabric samples were rinsed twice with warm distilled water and then cool distilled water to remove the adsorbed and unfixed finishing agents and followed by drying at ambient laboratory conditions. An unfinished cotton sample was used as a control.

2.2.9. Antibacterial activity

The antibacterial efficiency of the all fabrics was assessed according to pour-plate method. Gram-positive *S. aureus* and Gram-negative *E. coli* were used as the test microorganisms because they are the major causes of nosocomial infection in hospitals. Among surgical infections, 19% are caused by *S. aureus* and 11% by *E. coli* (Huang & Leonas, 2000). Antibacterial activity of the treated fabrics was evaluated as follows. Bacteria cells were precultured at 37 °C for 24 h. All the culture media were sterilized with normal autoclaving before being used.

The inoculum was made by direct suspension of colonies in saline solution with concentration of 8.9 g/L. It was adjusted to the turbidity of McFarland standard 0.5, or approximately 1–2 × 10^8 CFU/mL. Saline solution 8.9 g/L sodium chloride was used as the neutralizing solution. The suspensions were then diluted 1:1000 for *S. aureus* and 1:10,000 for *E. coli* in a fresh saline solution with the aim to achieve a cell concentration of 10^5 CFU/mL for *S. aureus* and 10^4 CFU/mL for *E. coli* as the inoculums in the test. TSA was applied as the agar. The glassware and test samples were sterilized in an autoclave at 121 °C for 20 min before experiments. All experiments were performed in triplicate against each tested microorganism.

The treated cotton fabrics and control sample (0.02 g) were cut into small pieces and transferred into a vial (10 mm × 100 mm). 1 mL of inoculum was added to each test tube. The test tubes were loosely capped to prevent evaporation and were placed in a temperature-controlled container at 37 ± 2 °C and then irradiated under a UVA lamp (Hitachi, TL05 8W, Japan, maximum intensity wavelength at 365 nm) for 3 h. The distance between light source and sample was set at 50 cm. Afterwards, 50 μL of the above adjacent–suspension was poured into sterilized Petri-dish and appropriate volume of TSA agar was added onto it. The plates were incubated at 37 °C for 24 h and the number of viable cells (colonies) was counted manually and the results after multiplication with the dilution factor were expressed as mean colony forming units (CFU) per mL after averaging the triplicate counts (number of colonies on plate × reciprocal of dilution of sample × 20 = number of bacteria/mL). It is assumed that one cell (or one cluster of cells) will multiply on the medium to produce a visible colony.

The antibacterial activity was expressed in terms of percentage of bacterial reduction after contact with the treated sample compared to the number of bacterial cells surviving after contact with the control sample. The percentage of reduction was calculated using Eq. (2).

$$R(\%) = \frac{(B - A)}{B} \times 100 \quad (2)$$

where A and B are the surviving bacterial cells (CFU/mL) for the plates containing treated and control cotton fabrics, respectively, after 3 h contact time under UVA radiation. $R(\%)$ is the percentage of bacterial reduction.

2.2.10. Fastness assessment

To evaluate the durability of sericin, NTO, and nanocomposite with or without different cross-linking agents on the fabrics against repeated launderings, treated fabrics were washed according to AATCC Test Method 61(2A)-1996. In this method, one cycle of laundering is equal to five launderings of medium or warm washing at 38 ± 3 °C. Each cycle lasted 45 min at 50 °C with 42 rpm and nonionic detergent. The fabric size used was 5 cm × 15 cm. In this study, all treated fabrics were subjected to 20 and 40 consecutive launderings. All fabrics were finally rinsed with distilled water thoroughly and dried at room temperature and then the antibacterial activity was measured.

2.2.11. Breaking strength assessment

The samples were conditioned for 24 h at 20 °C and 65% relative humidity before breaking strength testing. The breaking strength of the fabrics (weft and warp directions) was measured with a CRE tensile tester (Zwick 144660, Germany) on samples 10 cm length according to ASTM Method D 5035-2003. The testing was carried out at room temperature, and all recorded data were averages of four measurements.

3. Results and discussion

3.1. SEM analysis

The surface morphology of the untreated and treated cotton fabrics can be seen in Fig. 1(a)–(d). An obvious difference between the untreated and treated cotton fabrics was observed. These images demonstrated the presence of NTO and sericin on the coated cotton fabrics (Fig. 1(b)–(d)), whereas no such materials were seen for uncoated cotton fabrics (Fig. 1(a)).

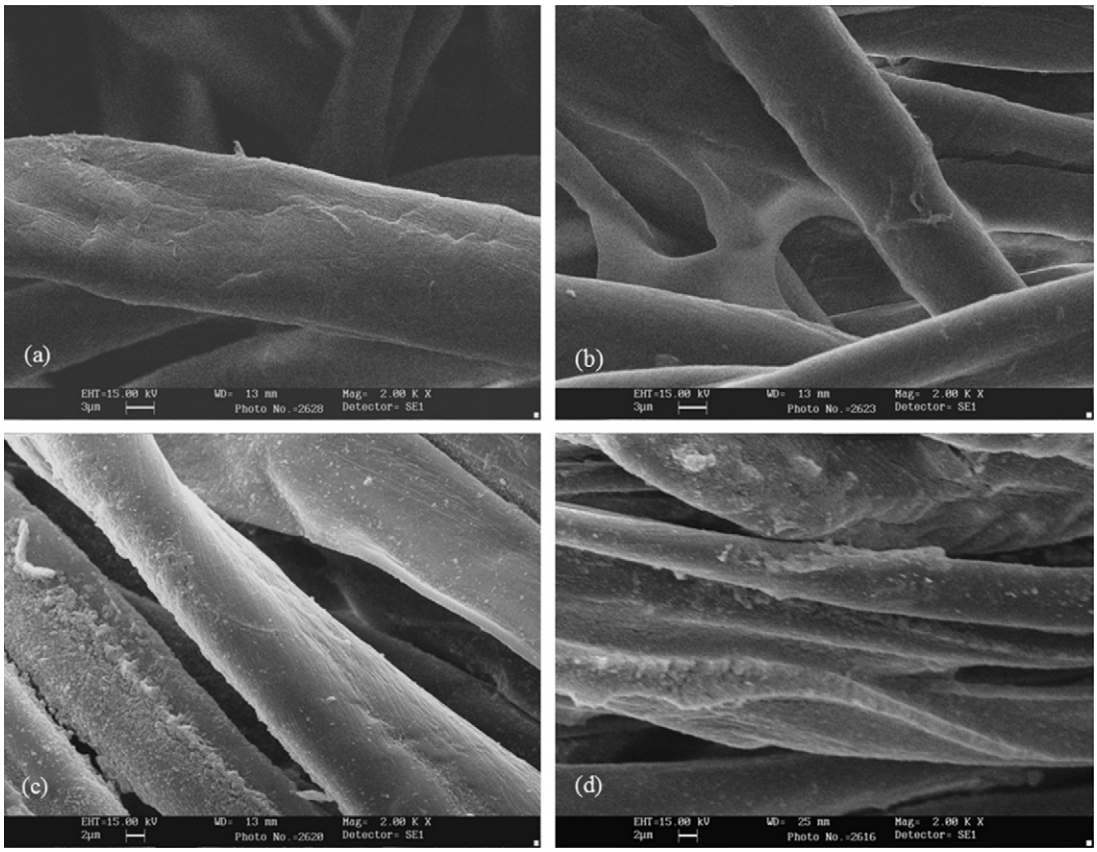

Fig. 1. SEM photographs of (a) untreated cotton, (b) N0S1X0, (c) N2S0X0, and (d) N2S1X0 (samples tested after 20 launderings).

The SEM images (Fig. 1(b) and (d)) showed that sericin macromolecules were bound on cotton fiber surfaces and there were also some sericin connections between two fibers suggesting that it acts like glue. Fig. 1(c) and (d) showed the formation of surface aggregates with particles greater than 30 nm in diameter that indicates the aggregation of NTO during finishing process. Also, these particles have formed relatively strong bonding with cellulose and hence were not removed during washing with warm water and detergent and only unbounded deposited particles may have been leached out.

3.2. EDX analysis

Fig. 2(a)–(c) shows the energy dispersive spectra of some samples treated with solutions containing NTO. It was indicated that there was titanium element onto the cotton fabrics treated with NTO and nanocomposite dispersion, suggesting that the NTO have been deposited onto treated cotton in addition to gold due to the gold coating layer. EDX analysis showed a peak at about 0.45 as energy position for titanium is located at 0.4522 suggesting its presence on the treated fabrics. Also, the peak for sample N2S1B2 is stronger than the other samples (N2S0X0 and N2S1X0). This means that more titanium deposited on the fabric treated with nanocomposite and cross-linking agent which can be attributed to strong interactions among nanocomposite, BTCA, and cellulose.

3.3. TEM analysis

A TEM image of NTO in Fig. 3(a) demonstrated irregularly shaped particles with diameters in the range of 20–30 nm. The small particles are believed to be anatase grains, while the big particles are rutile grains (Zhang, Wang, Zakaria, & Ying, 1998). Therefore the used NTO consists mainly of anatase with a minor component of rutile. The NTO in nanocomposite colloidal solution formed the agglomerates with nanoparticles greater than 30 nm (Fig. 3(b)).

3.4. XRD analysis

The XRD patterns of the untreated and treated cotton fabrics can be seen in Fig. 4(a)–(d). It is evident that all studied samples show remarkable crystalline peak at $2\theta = 22^\circ$, which is generally characteristic for cotton fabrics (Marchessault & Sundararajan, 1982). The intensity of the peak of cotton coated with nanocomposite became weaker compared to that of untreated cotton (Fig. 4(a) and (d)). This may be attributed to the presence of well-dispersed NTO on cotton which can protect the X-ray beam (Qi et al., 2006). Therefore the intensity of the peak related to cotton coated with nanocomposite became weaker.

It has been reported that sericin is an amorphous macromolecule (Gulrajani & Gupta, 1989, chap. 7). The X-ray pattern of the cotton fabric treated with sericin (Fig. 4(b)) does not show any distinct peak. This indicates that the extracted sericin powder is amorphous. For samples treated with NTO (Fig. 4(c) and (d)) sharper anatase peaks with greater intensities at 25.4°, 38.0°, and 48.0° were observed. The presence of brookite and rutile can be identified by peaks at 27.7°/31.1° and 27.5°/36.0°, respectively (Qi et al., 2006; Zhang & Banfield, 2000). No traces of brookite and rutile signs can be seen in treated samples, indicating that the TiO_2 nanoparticles in the finished fabrics might be existed in a mainly anatase state. This result agreed with the analysis from TEM image (Fig. 3(a)).

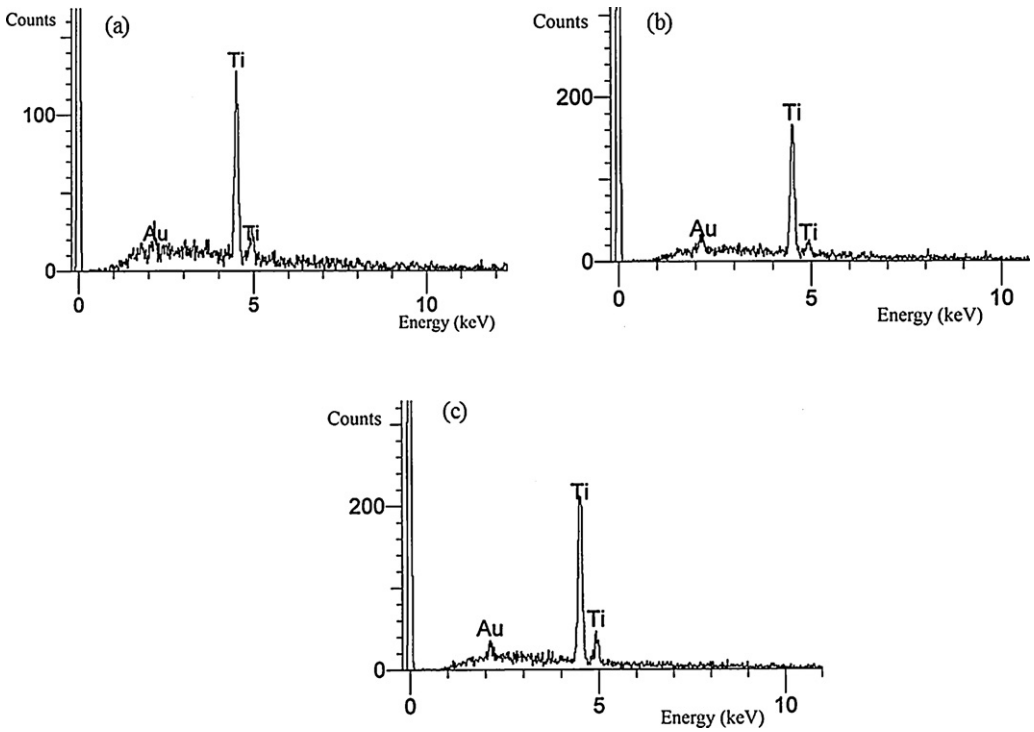

Fig. 2. EDX patterns of (a) N2S0X0, (b) N2S1X0, and (c) N2S1B2 (samples tested after 20 launderings).

3.5. FTIR analysis

Fig. 5(a) shows the IR spectrum of sericin powder. Sericin shows a peak between 1700 and 1600 cm^{-1} (1660.98 cm^{-1}) confirming the stretching vibration of the C=O. Peak at 1580–1510 cm^{-1} (1527.14 cm^{-1}) confirms the presence of the in-plane N—H bending. The peak at 3500–3000 cm^{-1} (3296.26 cm^{-1}) is associated with N—H stretching vibration. O—H stretching band is located at 3600–3200 cm^{-1} that overlapped with N—H stretching vibration peak at 3500–3000 cm^{-1}. C=O symmetry stretching is observed at about 1400 cm^{-1} (1396.41 cm^{-1}). The FTIR peaks of the sericin powder prepared in this study are similar to those of sericin powder obtained by other researchers (Gulrajani et al., 2008; Sarovart et al., 2003; Song & Wei, 2006).

Fig. 5(b) shows FTIR spectrum of untreated cotton. A broad peak corresponding to the O—H hydroxyl group of cotton fabric is observed at 3422.70 cm^{-1} and a peak of the C=O carbonyl group is observed at 1643 cm^{-1}. Asymmetric C—H stretching is obtained at 2129.24 cm^{-1}, whereas the symmetric peak is obtained at 2897.16 cm^{-1}. The characteristic vibration bands were observed at

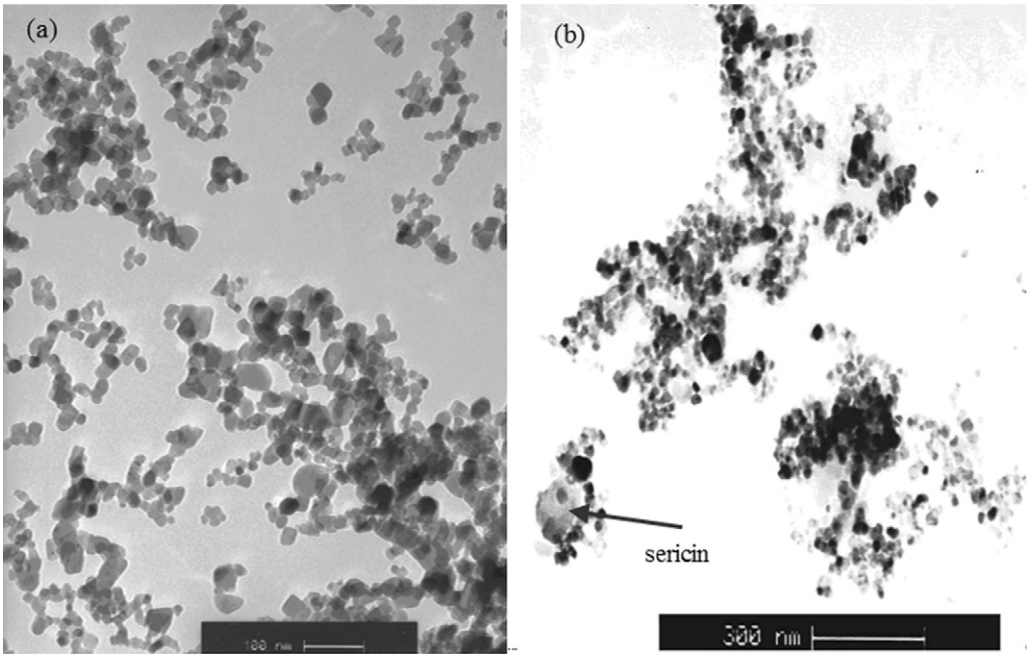

Fig. 3. TEM micrograph of (a) NTO powder and (b) nanocomposite colloidal solution.

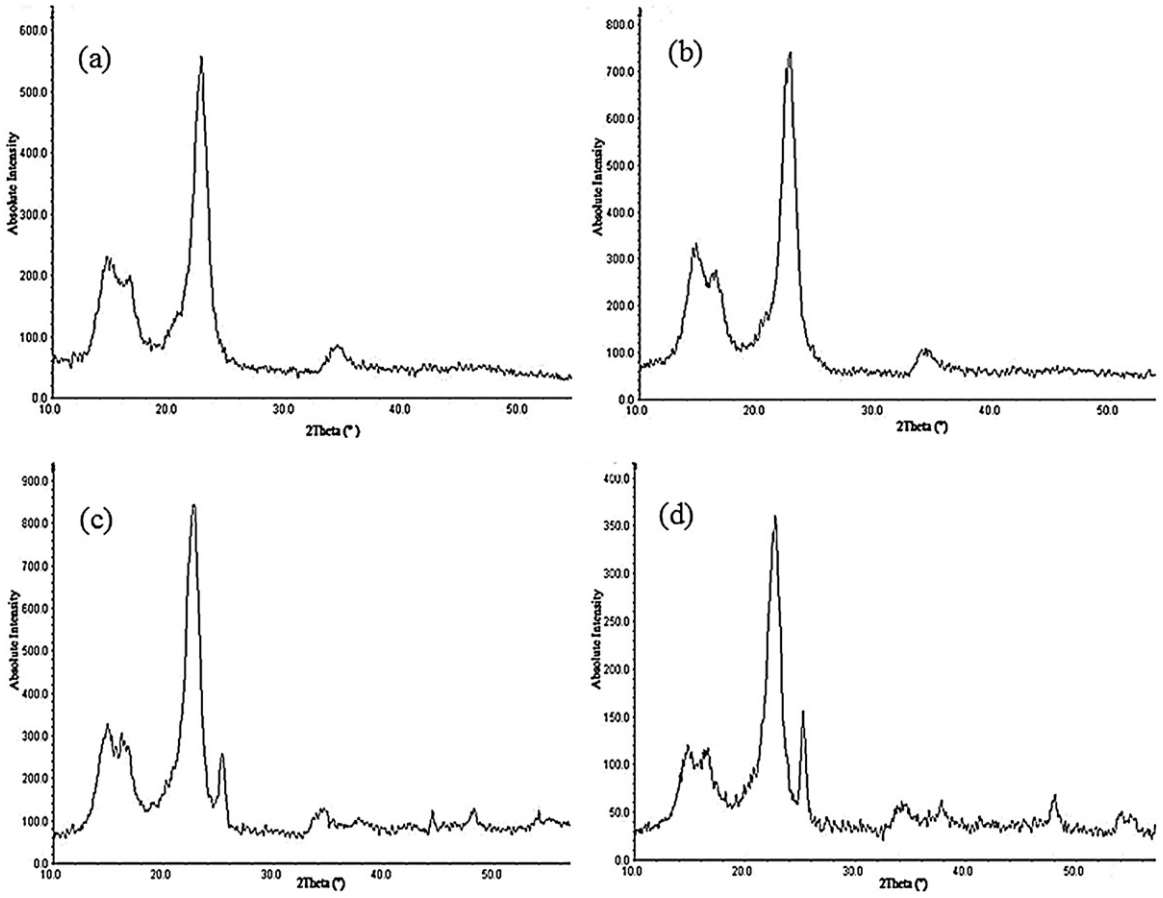

Fig. 4. XRD patterns of (a) untreated cotton, (b) N0S1X0, (c) N2S0X0, and (d) N2S1X0 (samples tested after 20 launderings).

1436, 1114, and 1057 cm^{-1} (1436.56, 1114.63, and 1057.08 cm^{-1}) which are characteristics for cellulosic structure (El-Shafei, Fouda, Knittel, & Schollmeyer, 2008; Hong & Sun, 2008; Hou, Zhou, & Wang, 2009; Nasr, Sayyah, Essa, Samaha, & Rabie, 2009).

Fig. 5(c) shows FTIR spectrum of cotton fabric treated with BTCA. The cotton fabric shows 1368.60 and 1435.51 cm^{-1} bands associated with symmetric stretching of carboxylate groups. A peak at about 1726.51 cm^{-1} attributed to the ester groups in linkage between cellulose and BTCA (Lee, Broughton, Akdag, Worley, & Huang, 2007; Yang, 1991).

Fig. 5(d) shows FTIR spectrum of the cotton fabric treated with nanocomposite and BTCA. The peak at 1525 cm^{-1} is related to carbonyl stretching peak. The peak at 3269.95 cm^{-1} corresponding to stretching vibration of the hydroxyl group of cellulose shifted to lower wavenumber, indicating a strong interaction between the hydroxyl groups of cellulose and NTO through hydrogen bonding interactions (Zeng, Li, Liu, & Zhang, 2011). This strong interaction could lead to the fixation of NTO onto the cotton.

3.6. Statistical analysis

After the cotton fabrics were treated with various finishing baths containing different concentrations of sericin, NTO, and BTCA or CA, the effect of these factors on the percentages of bacterial reduction against two bacteria strains; *S. aureus* and *E. coli* was evaluated. For samples treated with nanocomposite and different cross-linking agents, the analyses of variance (ANOVA) were performed which typically the fitted models obtained using various applied conditions and BTCA against two bacteria strains before and after 20 launderings were presented in Eqs. (3)–(6). Also, the response surfaces for samples treated with nanocomposite/BTCA were shown in Fig. 6 with the similar trend for samples finished with nanocomposite/CA. For unwashed samples, 25 g/L sericin, 50 g/L NTO, and 50 g/L cross-linking agents (samples N2S1X2) indicated 100% bacterial reduction for both bacteria strains. With the same laundering conditions, cotton treated with nanocomposite in sample N2S1B2 showed a higher antibacterial activity than sample N2S1C2. The samples treated with nanocomposite without cross-linking agents showed a weak durability confirmed by declined antibacterial activity. The maximum bacterial reduction with good laundering durability obtained on the fabric treated with 25 g/L sericin, 50 g/L NTO, and 50 g/L BTCA with 99.9% and 99.8% bacterial reduction after 20 launderings, and 98.8% and 98.3% bacterial reduction after 40 launderings for *S. aureus* and *E. coli*, respectively.

$$R\% = 82.10 + 26.70\,\mathrm{NTO} + 10.58\,\mathrm{sericin} + 4.53\,\mathrm{BTCA} - 7.83\,\mathrm{NTO}\cdot\mathrm{sericin} - 3.54\,\mathrm{NTO}\cdot\mathrm{BTCA} - 1.55\,\mathrm{sericin}\cdot\mathrm{BTCA} - 3.07\,\mathrm{NTO}^2 - 11.21\,\mathrm{sericin}^2 - 10.01\,\mathrm{BTCA}^2 \quad (E.\,coli/\text{before laundering}) \tag{3}$$

$$R\% = 84.50 + 23.68\,\mathrm{NTO} + 8.99\,\mathrm{sericin} + 6.00\,\mathrm{BTCA} - 7.35\,\mathrm{NTO}\cdot\mathrm{sericin} - 4.62\,\mathrm{NTO}\cdot\mathrm{BTCA} - 6.38\,\mathrm{sericin}\cdot\mathrm{BTCA} + 0.79\,\mathrm{NTO}^2 - 10.76\,\mathrm{sericin}^2 - 12.08\,\mathrm{BTCA}^2 \quad (S.\,aureus/\text{before laundering}) \tag{4}$$

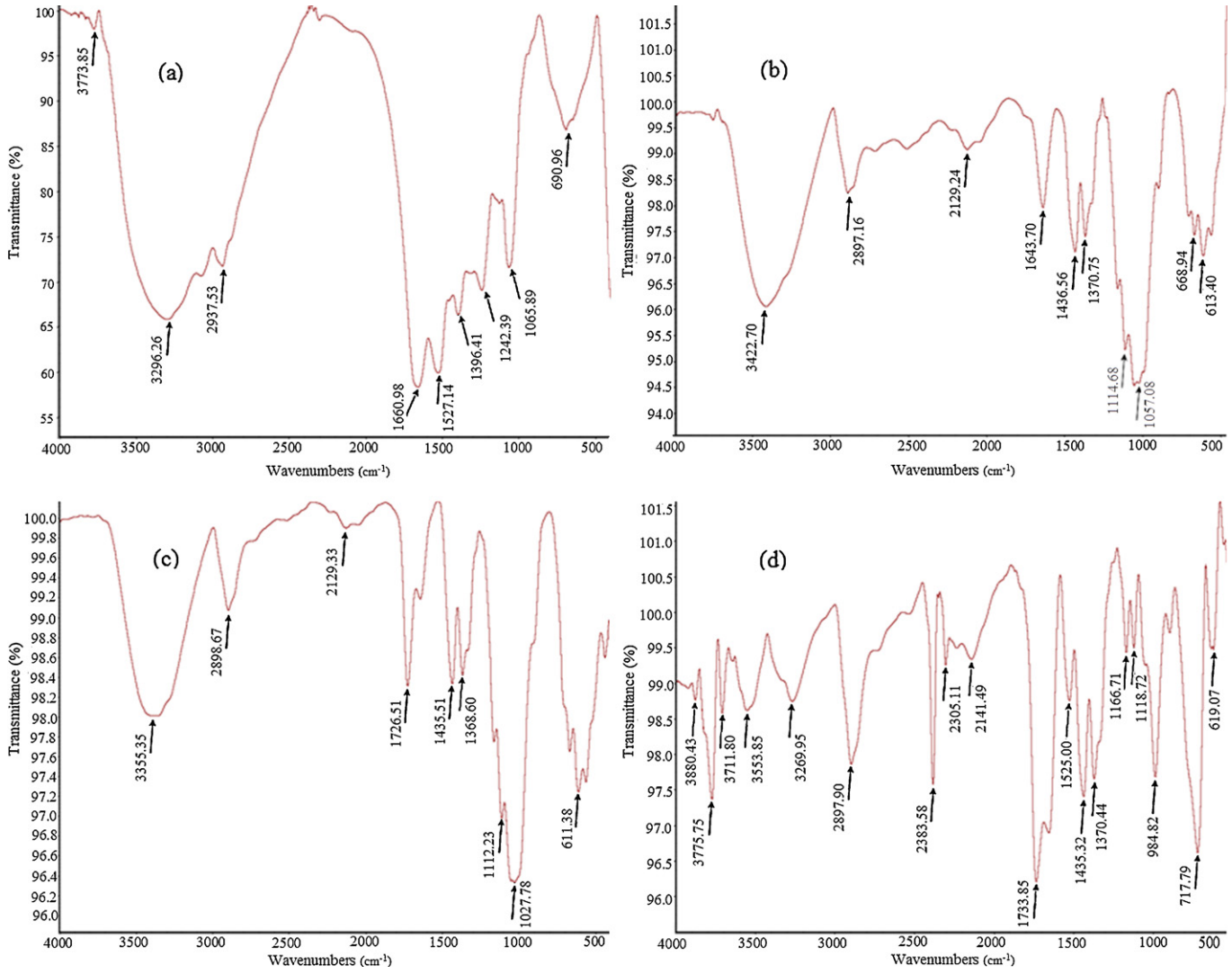

Fig. 5. FTIR spectra of (a) recovered sericin powder, (b) untreated cotton, (c) N0S0B2, and (d) N1S2B2 (samples b–d tested after 20 launderings).

$$R\% = 70.96 + 28.36\,\mathrm{NTO} + 5.68\,\mathrm{sericin} + 20.79\,\mathrm{BTCA} - 6.94\,\mathrm{NTO}\cdot\mathrm{sericin} + 0.67\,\mathrm{NTO}\cdot\mathrm{BTCA} + 3.75\,\mathrm{sericin}\cdot\mathrm{BTCA} + 1.21\,\mathrm{NTO}^2 - 22.24\,\mathrm{sericin}^2 - 25.43\,\mathrm{BTCA}^2 \quad (E.\ coli/\text{after 20 launderings}) \tag{5}$$

$$R\% = 71.80 + 26.87\,\mathrm{NTO} + 6.33\,\mathrm{sericin} + 22.99\,\mathrm{BTCA} - 6.33\,\mathrm{NTO}\cdot\mathrm{sericin} + 1.88\,\mathrm{NTO}\cdot\mathrm{BTCA} + 3.98\,\mathrm{sericin}\cdot\mathrm{BTCA} - 0.15\,\mathrm{NTO}^2 - 21.46\,\mathrm{sericin}^2 - 26.12\,\mathrm{BTCA}^2 \quad (S.\ aureus/\text{after 20 launderings}) \tag{6}$$

3.7. Antibacterial activity assessment

The influence of different treatment based on sericin and NTO alone and nanocomposite with or without cross-linking agents on the antibacterial activity of the cotton fabrics are given in Table 2. No bacterial reduction was found on the untreated cotton sample even a small increase recovered from the same sample after 3 h contact time, indicating *E. coli* and *S. aureus* use cotton as a nutrient.

The finished fabrics revealed different antibacterial activity depending on sericin, NTO, and cross-linking agent concentration in the finishing bath. However, all the treated fabrics almost showed good antibacterial property with higher activity by the fabrics treated with more NTO concentration (50 g/L).

The highest bacterial reduction can be seen for *S. aureus* in comparison with *E. coli* due to the very simple wall structure of the Gram-positive bacterium as compared with the very thick wall structure of the Gram-negative bacterium. This is facilitating the extent of oxidation and disruption of the cell, in turn giving better inactivation (Park, Kim, Nho, & Kwon, 1998) which determines their sensitivity to chemical agents (sericin, NTO, and cross-linking agents), namely; the antibacterial activity of treated fabrics is inversely proportional. Hence, the finished fabrics are more effective against Gram-positive than Gram-negative bacteria. Therefore, to achieve complete killing of bacteria, an appropriate concentration of finishing agents is necessary to obtain textile antibacterial finishing.

3.7.1. Effect of sericin on antibacterial activity

In acidic solutions, the amine group ($-NH_2$) in sericin becomes a cationic amine and allows the sericin to inhibit the growth of many bacteria. Numerous studies demonstrate that the antibacterial activity of sericin could be originated from its poly cationic nature which can interact with the negatively charged bacterial cell membranes (lipo-polysaccharides and proteins of microorganism

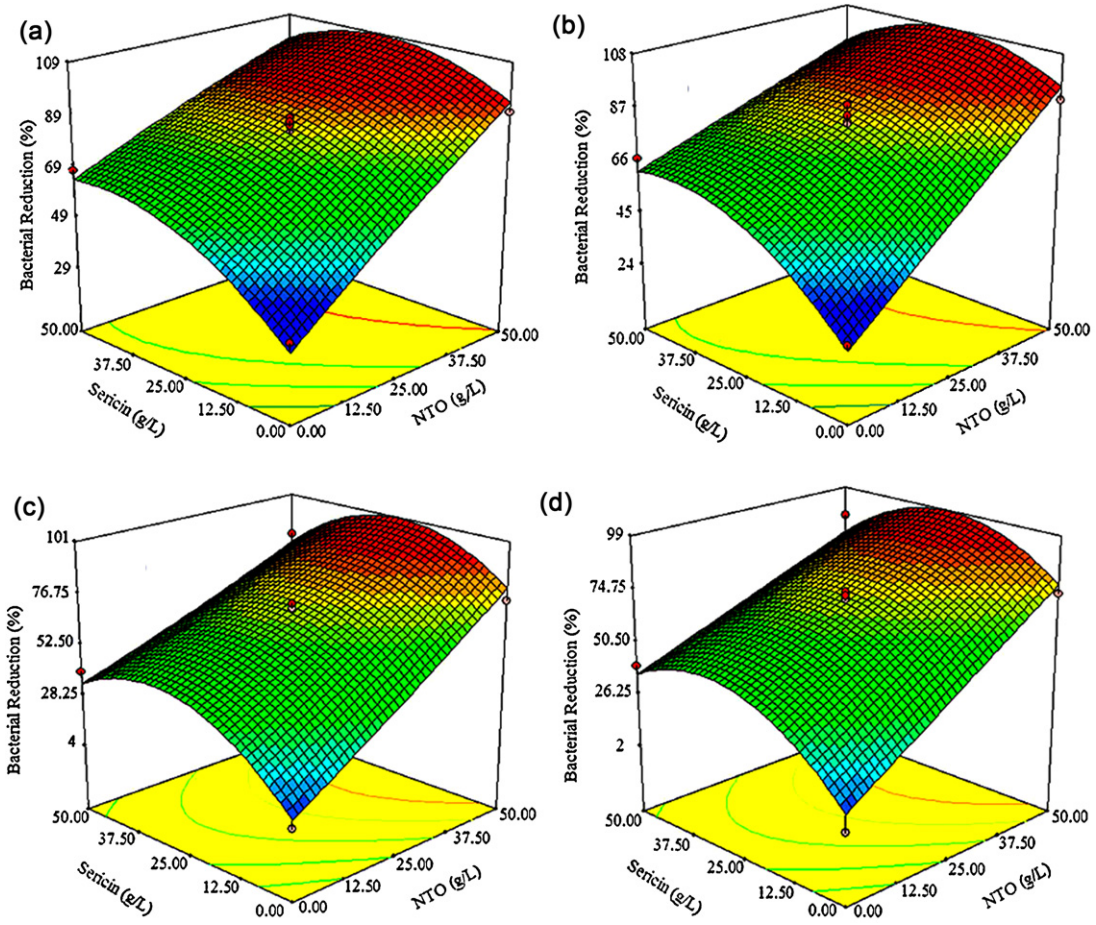

Fig. 6. Response surface graphs of percentage of bacterial reduction as a function of NTO, sericin, and BTCA concentration (a) *E. coli*/before laundering (b) *S. aureus*/before laundering (c) *E. coli*/after 20 launderings, and (d) *S. aureus*/after 20 launderings.

surface) resulting in changes in permeability which causes death of the cell by inducing proteinaceous leakage and other intracellular constituents of the bacteria cells (Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001; Lim & Hudson, 2004; Shahidi, Arachchi, & Jeon, 1999). On the other hand, sericin with low molecular weight can directly penetrate into the bacteria cells and complex with anion materials in cells. Consequently, the normal physiological activities of cells were interrupted and

Table 2
Bacterial reduction for various samples against two bacteria strains (before and after laundering).

Sample code	*R*(%) Before laundering				*R*(%) After laundering							
	Against *S. aureus*		Against *E. coli*		Against *S. aureus*				Against *E. coli*			
	X:BTCA	X:CA	X:BTCA	X:CA	X:BTCA		X:CA		X:BTCA		X:CA	
					20[a]	40	20[b]	40	20	40	20	40
N2S2X1	92.3	90.6	91.2	88.9	85.0	80.1	80.3	75.6	81.1	77.3	70.8	67.6
N1S1X1	80.4	80.1	80.7	79.9	72.1	68.5	63.2	61.7	70.2	67.1	60.2	55.9
N0S1X2	50.2	48.1	45.1	39.6	46.5	42.2	40.5	35.5	39.9	38.2	26.8	26.0
N1S0X0	43.7	40.9	42.5	41.8	9.5	6.3	8.9	6.5	7.9	6.2	8.5	7.7
N1S1X1	81.7	80.2	80.5	73.5	71.7	68.0	60.9	58.1	70.8	67.5	60.4	57.2
N2S1X2	100	100	100	100	99.9	98.8	99.3	98.0	99.8	98.3	98.1	97.7
N0S1X0	42.1	33.0	35.3	30.9	1.6	0.0	1.5	0.0	1.2	0.0	0.9	0.0
N1S1X1	84.0	83.4	83.1	81.0	70.1	68.1	64.0	60.6	68.1	67.0	62.9	55.3
N0S2X1	66.9	66.0	63.1	50.3	49.8	41.0	41.1	32.5	42.0	36.7	33.9	31.1
N2S1X0	100	100	100	100	52.3	42.6	46.2	39.5	47.7	40.9	40.9	40.0
N1S0X2	56.7	50.9	55.7	49.6	38.1	31.7	30.9	26.5	37.4	31.0	22.9	20.9
N1S2X2	76.0	68.2	65.9	62.5	46.8	42.7	39.2	37.6	46.3	40.7	35.6	32.1
N2S0X1	80.8	80.1	78.1	74.9	64.1	60.1	60.5	55.1	63.7	58.2	58.1	54.5
N0S0X1	27.6	19.8	26.4	16.3	2.6	0.4	1.2	0.0	1.9	0.0	0.7	0.0
N1S1X1	85.9	72.5	76.6	73.9	71.9	67.3	59.4	58.0	70.3	64.7	58.9	57.1
N1S1X1	87.0	80.7	79.4	75.9	73.9	67.0	62.1	59.1	70.2	66.8	57.5	57.0
N1S2X0	68.1	68.0	63.4	60.9	27.3	10.5	22.9	10.1	21.9	10.0	17.7	10.2

[a] Bacterial reduction after 20 cycles.
[b] Bacterial reduction after 40 cycles.

the bacteria were finally killed (Shi et al., 2008). In this study, the used method for sericin extraction was hot water which followed by evaporation in order to concentrating. This process may cause hydrolysis of sericin and lowering molecular weight of sericin (Oh et al., 2011), thus both mechanisms might be considered for antibacterial activity of sericin.

The higher antibacterial activity of the finished fabrics was observed as the sericin concentration increased to 50 g/L (Table 2). In fact, the linkage of cationic compound such as sericin to cotton substrate is mainly by ionic interactions between poly cationic sericin and anionic cotton surface as well as covalent bonding between sericin and cotton via intermediate of cross-linking agent.

3.7.2. Effect of NTO on antibacterial activity

A number of researches have shown that typical bacteria such as *E. coli* and *S. aureus* can be effectively killed by the cellulose treated with TiO_2 under UV irradiation (Daoud, Xin, & Zhang, 2005; Kangwansupamonkon, Lauruengtana, Surassmo, & Ruktanonchai, 2009). The samples treated with NTO after UVA exposure exhibited good antibacterial activity against both bacteria, especially at higher concentration. At 3 h contact time with the same concentration, the cotton fabrics treated with NTO suspension had greater antibacterial activity than the sericin treated samples. Similar findings have been reported a significant reduction in the bacteria cell count of TiO_2-coated cellulose under UV irradiation (Daoud et al., 2005).

After samples treated with NTO and nanocomposites containing NTO have been irradiated UVA and activated, it could be suggested that reactive oxygen species (ROS) such as $^{\bullet}OH$, $^{\bullet}O_2^-$, $^{\bullet}HO_2$, and H_2O_2 generated on the TiO_2 surface. In addition, produced photo holes have great potential to oxidize organic species directly or indirectly via the combination with water and OH^- on the surface of TiO_2 (Fujishima, Rao, & Tryk, 2000; Gaya & Abdullah, 2008). Photo holes and ROS production may break down the cell wall and outer membrane of bacteria cells. This allows cell contents to leak out and NTO to enter, thereby causing cell irregularities and depressions. It should be mentioned that the outer membrane, the outermost layer of the cell wall, contains phospholipid, lipo-polysaccharide, and protein as major constituents (Sunada, Watanabe, & Hashimoto, 2003) which produced ROS may attack and decompose polyunsaturated phospholipids in bacteria cells (Maness et al., 1999).

An important parameter in the photo catalytic reactions taking place on particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photo catalyst and size of aggregates formed (Bahnemann, Muneer, & Haque, 2007). Under acidic or alkaline condition the surface of TiO_2 can be protonated or deprotonated respectively according to the following reactions (Eqs. (7) and (8)):

$$TiOH + H^+ \rightarrow TiOH_2^+ \quad (7)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \quad (8)$$

Thus, TiO_2 surface will remain positively charged in acidic medium (pH < 6.9) and negatively charged in alkaline medium (pH > 6.9). TiO_2 is reported to have higher oxidizing activity at lower pH (Sun et al., 2006). In this study, the acidic medium was attained by acid character of the cross-linking agents and NTO.

3.7.3. Effect of cross-linking agents on antibacterial activity

The cotton fabrics treated with BTCA and CA were fairly effective against both tested bacteria. Bacteria need a physiological pH inside their cells and most of them grow best in the pH range of about 6–8 and will not grow at pH levels below 4.6. In general, bacteria survive at an alkaline pH better than at an acidic pH (Orhan et al., 2009). Consequently, lower pH levels of the cross-linking agents at different concentrations caused more antibacterial activity however, they were especially more effective against *S. aureus* than *E. coli*. When similar experiments were performed with or without cross-linking agents, the finishing agents along with a cross-linking agent were more effective against both bacteria. On the other hand, carboxyl groups having strong polarity can react with phospholipids in the cell membranes. The cell membranes will be broken because of the strong electrostatic interaction and result in the death of cells (El-Shafei et al., 2008). It seems that the cross-linking agent type could affect the antibacterial activity because the activity of the fabrics treated with various cross-linking agents was relatively different.

3.7.4. Effect of nanocomposite on antibacterial activity

The activity of the bacteria cells decreased by the presence of both NTO and sericin as indicated in Table 2. All nanocomposite treated fabrics showed high antibacterial activities with more than 60% bacterial reduction at 3 h contact time. The best processing conditions for optimal antibacterial activity was 50 g/L NTO, 25 g/L sericin, and 50 g/L cross-linking agent.

The effective antibacterial activity may be explained by a two-step process. The first step is the partial decomposition of the outer membrane in the cell envelope by (1) a photo catalytic reaction in which reactive oxygen species can induce oxidative damage in outer membrane (Sunada et al., 2003) and (2) under acidic conditions, the primary amine groups provide positive charges which interact with negatively charged residues on the surface of bacteria. Such interactions cause great changes in the cell surface and cell permeability, leading to leakage of intracellular substances (Lim & Hudson, 2003). This step is followed by the permeation of NTO and sericin with low molecular weight into the cytoplasmic membrane. Therefore, the second step is a disorder of the cytoplasmic membrane caused by the penetrated chemical materials, which results in a loss of the cell's integrity.

There was a general antibacterial activity enhancement on the most nanocomposite treated samples compared to the samples treated with sericin or NTO alone. This can be proposed by the following reasons:

(a) The electron–hole induced by photo catalysis might be filled with ions (mainly Na^+) in inoculums through the antibacterial test. However, the $-NH_2$ functional groups of the sericin prevent rejoining of the electron–hole on the NTO surface with ions in inoculums (Shi et al., 2008). In fact, sericin is the protein capable to absorb minerals (Sasaki, Kato, et al., 2000; Sasaki, Yamada, et al., 2000);
(b) The photo catalytic activity of NTO can be lowered remarkably by the Na^+ ions diffused from inoculums into NTO to form inactive $NaTiO_3$ (Fujishima & Rao, 1997). On the other hand, sericin contains high amount of serine (hydroxyl group) and aspartic acid (carboxyl group) causing chelation between the hydroxyl/carboxyl groups with elements (Sasaki, Kato, et al., 2000; Sasaki, Yamada, et al., 2000) prevented formation of inactive $NaTiO_3$;
(c) In nanocomposite containing sericin and NTO, cationic sericin could bind to bacteria cells and encourage more NTO toward cells due to interactions between sericin and NTO. Therefore, the content of chemical agents affecting the bacteria cells in nanocomposite samples might be more in comparison with samples treated with sericin or NTO alone.

The antibacterial activity of the fabrics was enhanced further by increasing NTO concentration to 50 g/L and sericin to 25 g/L, especially against *S. aureus* (Table 2). The activity decreased

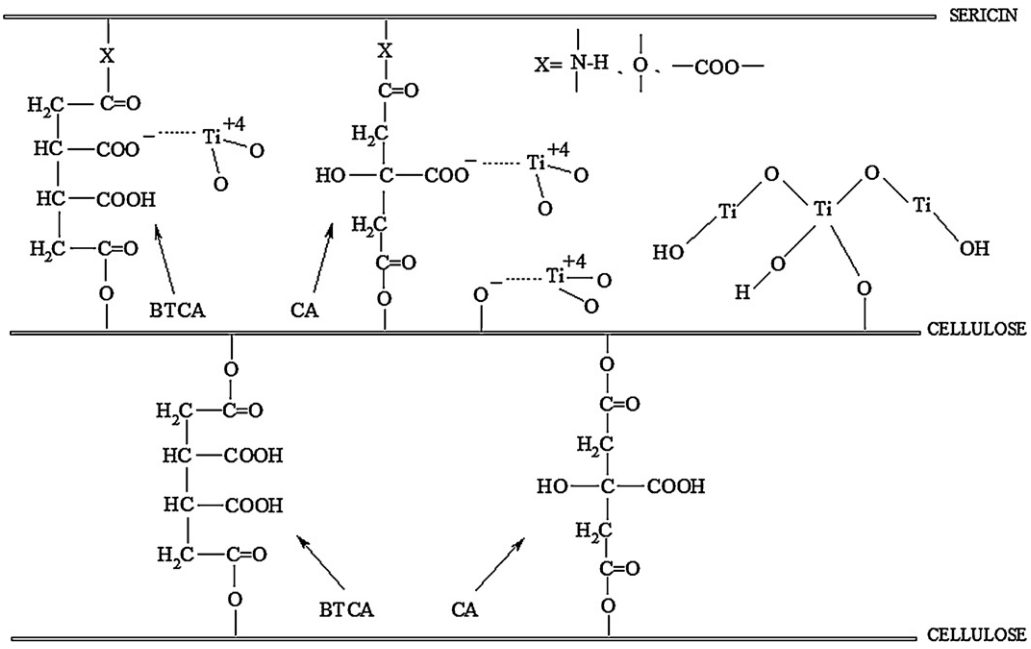

Fig. 7. Schematic of dominant forces between various ingredients of nanocomposite and cotton.

somewhat in the nanocomposite with increased sericin to 50 g/L due to:

(a) Coating of NTO surface by sericin macromolecules and consequently reducing ROS generation;
(b) Action of sericin as a ROS scavenger (Fan, Wu, Chen, Mao, & Ren, 2009);
(c) Coverage of bacteria surfaces by sericin macromolecules resulting in leakage decrease of intracellular substances especially when sericin was not effectively cross-linked to cellulose;
(d) Inhibition of peroxidation of bacteria cell lipids by high amounts of sericin (Kato et al., 1998).

For samples N2S1X2, N2S1X0, and N2S2X1, a high reduction of bacteria occurred on the unwashed fabrics. Overall, an increase of the antibacterial activity for nanocomposite was observed however, the increase can be depended on the variety of the bacterium as well as on the amount of the sericin and NTO used.

3.8. Laundering durability

To evaluate the durability, the samples were washed for 20 and 40 cycles, and the results were shown in Table 2. The cotton fabric treated with nanocomposite showed broad-spectrum antibacterial activities against two bacteria strains.

Table 2 shows the decrease in the activities of the treated fabrics without the cross-linking agents compared to those fabrics treated with the cross-linking agents. The durability against laundering of sample treated with BTCA was higher than CA; greater antibacterial activity was especially seen against *S. aureus* than *E. coli*. Higher bacterial reduction for samples treated with BTCA was expected due to having four carboxyl groups capable cross-linking three cellulosic chains and sericin macromolecule. On the other hand, a light yellowing has been reported on the cross-linked cotton with CA. Consequently, adding BTCA to the antibacterial finishing would be a better choice in imparting durable antibacterial activity to cotton fabrics.

The stability of the NTO on cotton was studied by comparing antibacterial activity of treated cotton fabrics before and after laundering (Table 2). The activity was maintained relatively high after laundering (N2S0X1), indicating good adhesion between the NTO and cotton, which may be attributed to the formation of covalent bonding resulting from the dehydration reaction between the hydroxyl groups of the cotton and the hydroxyl groups of the NTO (Daoud & Xin, 2004; Daoud et al., 2005). Furthermore, BTCA and CA can maintain NTO through ionic interaction between carboxylate anionic groups related to polycarboxylic acid and NTO cation (Nazari et al., 2010; Yuranova, Laub, & Kiwi, 2007).

On the other hand, the water-soluble sericin can be remarkably removed from the fabric after consecutive launderings, because there are no chemical bonds with fabrics (N0S1X0). However, it could be fixed on the cotton fabrics covalently with intermediate of cross-linking agents which causes better laundering durability (N0S2X1 and N0S1X2).

The antibacterial activities of the fabrics treated with different nanocomposites (especially N2S1X2) and cross-linking agents (especially BTCA) after laundering were relatively unchanged compared to those of the fabrics treated with sericin or NTO alone. BTCA and CA can produce a cyclic anhydride as a result of heat and catalyst. This could result in a cross-linking between cellulose and sericin as well as cellulosic chains (Montazer & Gorbanali-Afjeh, 2007). The chemically dominant forces and interactions between various ingredients of nanocomposite and cellulosic chains are summarized as follows and the schematic of main forces is illustrated in Fig. 7:

(a) Covalent bonding between the carboxyl groups of cross-linking agent as an intermediate and the functional groups of sericin (mainly hydroxyl and amine groups) and the hydroxyl groups of the cotton;
(b) Covalent bonding resulting from the dehydration reaction between the hydroxyl groups of NTO and the hydroxyl groups of the cotton;
(c) Ionic interaction between the negatively charged carboxyl groups of cross-linking agent (as well as hydroxyl group in CA) and positively charged NTO;
(d) Ionic interaction between the negatively charged cotton and positively charged NTO.

(e) These interactions and bonding are relatively strong resulted just a small change in antibacterial activity of the treated samples with given nanocomposites after repeated launderings.

3.9. Breaking strength analysis

The breaking strength of the untreated cotton fabric was 44.201 kg and decreased for fabrics finished with NTO alone (36.784 kg for N2S0X0, 31.070 kg for N2S0B1 and 32.964 kg for N2S0C1). In fact, radical reactions due to ROS generation can affect the cellulose backbone and lead to a decrease in the degree of polymerization and eventually to a drop in the breaking strength (Buschle-Diller, Inglesby, El-Mogahzy, & Zeronian, 1998). The mechanical strength of cotton cross-linked with BTCA and CA affected adversely (24.134 kg for N0S0B2 and 29.980 kg for N0S0C2) which this can be attributed to irreversible acid degradation. Therefore, the breaking strength decreased dramatically, depending on the increasing acid concentration after the polycarboxylic acid treatment. This could be associated with lower acidity (the stronger the acid was, the greater the damage was) (Kim, Nam, Choi, & Jinho, 2003). However, the addition of SHP as a catalyst contributed to enhancing the strength retention of the cotton (Orhan et al., 2009). The results for the cotton fabrics treated with BTCA and CA in the presence of sericin showed better strength than those treated with the polycarboxylic acids alone (43.412 kg for N0S1X0, 30.955 kg for N0S1B2 and 32.332 kg for N0S1C2). This could be associated with a higher pH of the finishing solution. The fabrics finished with nanocomposite did not dramatically affect the breaking strength of the fabrics due to presence of sericin (ROS scavenger), SHP, and dispersing agent resulted in higher pH (40.693 kg for N2S1X0, 33.638 kg for N2S1B2 and 37.731 kg for N2S1C2).

4. Conclusions

Cotton fabrics were modified with sericin/NTO nanocomposite and its components alone in presence or absence of two polycarboxylic acid cross-linking agents using pad-dry-cure technique. The finishing treatment was more effective against *S. aureus* than *E. coli*. Evaluation of antibacterial activity at 3 h contact time resulted in complete or relative sterilization of the tested bacteria in all the samples except control one. For each bacteria strain, the antibacterial activity of the fabrics treated with NTO or sericin was not high, especially at low concentration, however, the activity was enhanced for fabrics treated with some nanocomposites. Therefore, the present study provided evidence for the antibacterial effect of the nanocomposite especially at higher concentrations of NTO against common hospital pathogens; *S. aureus* and *E. coli*.

This study indicated that an optimum bacterial decomposition for textiles application was achieved by the cotton fabrics treated with N2S1X2. The prepared specific nanocomposite had "synergistic effect" for antibacterial activity against two bacteria strains. The degree of bacterial reduction is directly related to pH, type and concentration of cross-linking agent, sericin, and NTO.

The breaking strength of fabrics treated with sericin alone has not been considerably changed whereas dropped for fabrics treated with NTO alone due to ROS generation as well as fabrics treated with polycarboxylic acid cross-linking agents due to irreversible acid degradation. The fabrics finished with nanocomposite did not adversely affect the breaking strength of the fabrics. This can be attributed to presence of sericin (ROS scavenger), SHP, and dispersing agent led to higher pH.

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